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Attention: Dr. R. S. Miller (Code 1132P)

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Subject: Third Quarterly Summary of Progress on Contract
"Energetic Thermoplastic Elastomer Synthesis"
Covering Period 01 November 1987 to 31 January 1988,
Contract N00014-87-C-0098

Dear Dr. Miller:

Enclosed is our SPIE/O-E LASE paper presented at the International Society for Optical Engineering Optoelectronics and Laser Application 88 Meeting in Los Angeles, California, on January 14, 1988. In addition to this paper is the most recent evolution of the synthesis technique and a list of samples prepared and sent to the Naval Weapons Center to initiate the structure/property relationship study. These serve as the subject report.

Energetic Thermoplastic Elastomers

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ABSTRACT

The objective of our research is to synthesize energetic polyether binders with the ability to undergo reversible physical crosslinking at temperatures compatible with high energy propellant ingredients. Commercially available thermoplastic elastomers fail to meet our criteria because of excessively high processing temperatures and melt viscosity, high modulus and low stress/strain capability. It was proposed to synthesize ABA type block polymers with the A blocks being polymers able to form crystalline structure (as opposed to glasses) having a sharp melting point of 85-95°C. This would enable phase miscibility in the melt, thus lowering melt viscosity, and reduce creep close to the melting point. ABA structures were chosen over (AB)_n, enabling low molecular weight polymers to be synthesized, again lowering viscosity.

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In order to successfully achieve our objectives, it was necessary to synthesize precise polymer structures with little deviation from the required structure. After evaluating blocklinking techniques, we decided to employ living cationic polymerization with systematic monomer addition. To this end, we have examined numerous catalysts and co-catalysts. Our research at this time is centered on bis cumyl chloride/silver antimony hexafluoride in which we see promising results. The effects of polymerization temperature, catalyst formation, catalyst concentration, rate of monomer addition and monomer concentration were determined with respect to molecular weight control and structure. Polymer workup and purification, a problem in our initial studies, has been resolved.

We have now synthesized polymers varying in molecular structure and correlated the resulting physical properties to structural changes. The effect of structure and molecular weight on melt viscosity and morphology is now being examined.

1. INTRODUCTION AND BACKGROUND

The major deficiencies of current state-of-the-art binders can be overcome through the use of thermoplastic elastomers. The binder problems encountered include, but are not limited to, the use of nonenergetic binders, high end-of-mix viscosity, thermally labile urethane linkages, long or inconsistent cure, nonreversible processing, toxic chemical curatives, and extreme vulnerability to unscheduled detonation. At the initiation of this research effort it was clear to us that development of a new generation of polymeric binders, that were themselves energetic and physically crosslinkable with the added advantage of potential molecular modeling to end uses, would alleviate these problems.

Thermoplastic elastomers (TPE) are block copolymers with the property of forming physical crosslinks at predetermined temperatures. The classical TPE obtains this property by having one of the component block's glass transition point above room temperature, as typified by "Kraton". Thus, at temperatures below 110°C the glassy block forms glassy domains in the continuous butadiene phase and physically crosslinks it. In order to form these glassy domains the styrene block must be immiscible in the melt phase, thus causing extremely high melt viscosities.

In our original concept we proposed¹ to form TPES from polyether glycols that have similar structural properties and would derive the physical crosslinking from the formation of crystalline domains. It is significant to replace the amorphous glassy blocks with crystalline blocks. Basic thermodynamic incompatibility between the two blocks is not required for phase separation because of the heat of fusion of the crystalline block. Perhaps the most important advantage of the crystalline block is that the melt viscosity will decrease more rapidly on increasing the temperature above the melting point of the crystalline block.



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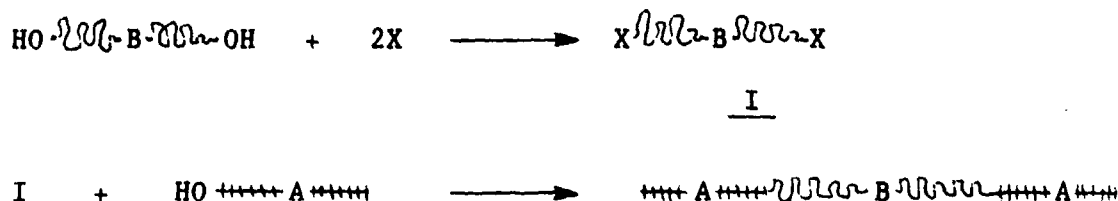
Therefore, we embarked upon the synthesis of two distinct series of polyether glycols.

1. Polymers that were crystalline in nature with melting point temperatures of 85 to 95°C.
2. Polymers that were amorphous in nature with glass temperatures of less than -40°C.

From our previous work^{1,2} we had synthesized poly[bis(ethoxymethyl)oxetane] (BEMO), and poly[bis(azidomethyl)oxetane] (BAMO), both of which were crystalline and melted within our required melting point range. BAMO, being energetic, was selected for this program. For use as a soft block we selected poly[3-azidomethyl-3-methyloxetane] (AMMO), an amorphous polymer, and its random copolymers with BAMO. Other amorphous polymers will be included at a later date.

Each monomer was then used to synthesize a series of polymers of varying molecular weights to gage the effect of molecular weight and phase compatibility of the individual blocks. It was found that homoBAMO formed crystalline polymers at relatively low molecular weight (~3,000) and that increasing the molecular weight to over 100,000 had very little effect on the melting point. AMMO and its random copolymers with BAMO were evaluated as soft blocks. HomoAMMO is a clear, flowable oil even at high molecular weight, with a glass point below the program objectives. 50/50 BAMO/AMMO, if correctly made, is similar in properties. Copolymers of above 70/30 BAMO/AMMO tend to have a crystalline component, probably due to the fact that enough runs of homoBAMO exist causing some degree of crystallinity.

Now that a number of polymers of each block component had been synthesized, we considered block linking to gage how interactions of blocks would effect the physical characteristics of each block. To this end we examined the use of urethane and carbonate blocking techniques. The overall synthesis technique simply takes the center block, which has a hydroxyl functionality, endcaps it with either a diisocyanate or phosgene, then two equivalents of the crystalline end block are added.



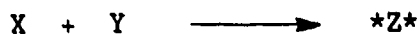
The physical and mechanical properties of these polymers were then extensively examined, and a number of encouraging observations were made.³

1. The blocks were completely compatible in the melt phase in all molecular weights examined.
2. The BAMO blocks readily crystallized from the melt down to 3,000 molecular weight in 45,000 center block molecular weight.
3. Morphology (spherulite size) was dependent of the temperature at which the TPE was allowed to crystallize (smallest size grew at 10°C below the melting point).
4. The rate of crystallization increased as the BAMO block size increased.
5. The glass point of the center block was not changed by incorporation into the block polymer.
6. The melting point of the BAMO block could be sharpened and raised 3-8°C simply by heating the "cured" TPE slightly below its melting point for one hour (annealing).
7. Potential mechanical properties, after optimization of block size and block ratio, would appear to meet program goals.

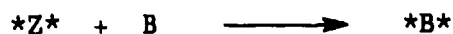
The most important observation was, in fact, that the block linking technique did not and probably would not produce the high degree of structural definition required for our molecular modeling studies. After extensive structural analysis we concluded that we were, in fact, synthesizing $(AB)_n$ polymers between $N = 1$ and $N = 3$, approximately 40% of the total being $N = 1$ (AB) which, in fact, will not exhibit thermoplastic elastomeric properties. Therefore, we embarked on an examination of an alternative synthesis route employing the living polymer characteristics of cationic polymerizations.

In this scheme a living polymerization center is formed and the monomers are added in sequence to form the required structure.

Initiation of a Dication



Propagation Step I



Propagation Step II



Termination



The rationale behind this synthesis scheme is that if all self termination reactions during propagation are removed, then the final polymer structure reflects the monomer stream sequence and the final structure will be an ABA sequential block polymer.

Our first attempt at the sequential polymerization technique employed the preinitiator derived from butane diol and boron trifluoride.⁴ We found that the nonenergetic oxetanes, being significantly faster to propagate than the energetic monomers, formed block polymers. The latter did tend to block merge to form more of a gradient copolymer. This we felt was entirely due to the rate of monomer uptake and that the concept of sequential polymerization was well founded. In order to form well-defined blocks with minor or no diffused block interfaces, we would have to find cationic initiators and/or counter ions that increase the rate of propagation by orders of magnitude so that no lag in monomer uptake takes place.

2. RESULTS AND DISCUSSION

Surveys of recent literature revealed a considerable volume of work by J. P. Kennedy on the quasiliving carbocationic polymerization of isobutylene⁵, α methylstyrene, and others. This method to generate a living cationic initiator employs the co-catalyst bis cumyl chloride (BCC) with selected known catalysts; e.g., BF_3 , ASF. Reviewing this excellent literature, it immediately appeared that this system could solve our problems. The preinitiator apparently causes initiation rapidly, and the counter ion from silver antimony fluoride is known to favor rapid propagation. Added to this, it was our opinion that this was a dicationic initiator which would greatly simplify our synthesis route. We therefore set about evaluating the system.

We first took the monomer, 3,3-bis(ethoxymethyl)oxetane [BEMO], and polymerized it by our standard technique⁴, substituting BCC/ASF for BF_3 /BDO. It was immediately apparent that the polymerization was complete in minutes instead of hours. It was also obvious that every aspect of our technique (solvent, temperature, rate of monomer addition, how the initiator is formed) and workup was not adaptable to this new system. Therefore, we examined and adapted significant changes to the polymerization technique with respect to the above parameters.

First, we examined the formation of the adduct of BCC and ASF. We found that the initiator must be made at temperatures less than -80°C . At temperatures above -80°C a blood red color is formed followed by rapid homopolymerization (assumed by fortuitous free radical polymerization) of the BCC. Even if the preinitiator is formed at -95°C (pale yellow color) and allowed to warm up, the result is the same. We believe that the homopolymerization still occurs at -95°C but is only, at best, mildly competitive with the oxetane initiation. Because of this last observation we now place the ASF in the reactor, cool to -95°C , then inject a solution of the BCC at the start of the monomer addition. We find this minimizes homopolymerization of the BCC.

We have also found that the preinitiator concentration is very critical to the polydispersity and predicted molecular weight of the resulting polymer. A concentration of less than $2 \cdot 10^{-3}$ molal solution produces the best polymer, as shown in Table 1.

Table 1. Effect of Preinitiator Concentration on Molecular Weight Distribution

Preinitiator Concentration (Molal)	Polydispersity (Q)	M_n/TM_n
$9 \cdot 10^{-3}$	4.0	4.8
$5 \cdot 10^{-3}$	2.5	3.8
$2 \cdot 10^{-3}$	1.4	3.2
$1 \cdot 10^{-3}$	1.3	3.0

TM_n = Theoretical Molecular Weight

This data clearly shows that only 30% of the BCC initiates polymerization; therefore, 70% is assumed to be consumed by homopolymerization.

An equally critical technique is how the monomer is added to the reactor. As pointed out by Kennedy, it is extremely important that the monomer is added in a continuous stream. This directly affects the symmetry of the molecular weight distribution. Dropwise addition causes dramatic broadening of the distribution. As important is the rate of addition. Using oxetane monomers, the rate of addition should not fall below 20% of the total monomer to be added per minute. This means that the whole synthesis is complete in five minutes. Even at this rate, no monomer is detected in the reactor during monomer addition. Obviously, we were concerned about polymerization exotherm at this addition rate. By precooling the monomer (heat exchanger coil in the injection tube) and maintaining the reactor cooling bath at -95°C , the polymerization temperature could easily be maintained at -85°C . This was found to be quite adequate to produce good block polymers.

Quenching the reaction after complete monomer addition with aqueous methyl alcohol at -95°C was found to be effective. The pale yellow solution immediately turned colorless. Working up the polymer at this point became a severe problem. It was found, after warming to room temperature, that the catalyst was reduced to a colloidal suspension which turned black on minimal exposure to light (silver salts). Washing with base (NaHCO_3 , our normal technique) and water followed by filtration had no effect. Warming to coagulate the solid and washing with various strengths of hydrochloric acid were equally ineffective. After considerable effort, including centrifuging, we found that 0.88 ammonium hydroxide dissolved the silver salts and reduced the antimony ammonium salt to an easily filterable solid. After washing with water followed by drying, the final polymer was precipitated from methyl alcohol.

The development of this technique and the fine tuning has been an iterative effort with the Naval Weapons Center. The analysis/characterization effort was carried out by this group under the direction of Geoffrey A. Lindsay. Robin A. Nissen has examined the polymers for molecular structure and degree of blocking by NMR techniques. BY FT-IR Melvin P. Nadler has examined structure of the crystalline blocks and aided us on the effort of block size and rate of crystallization. Molecular weight was measured by Low Angle Light Scattering and Gel Permeation Chromatography by Mostafa Talukder. By this cooperative effort we have now produced a series of triblock azido thermoplastic elastomers with extremely promising potential for our application objectives. A detailed account of the NWC characterization effort has been reported at the 1987 JANNAF Propulsion Meeting.

Now that we can synthesize triblock polymers of very specific structure, we have begun to vary the block sizes relative to each other. We will evaluate the effect on modulus, stress and strain on these changes and fully expect to be able to molecular model the polymer to specific mechanical properties once these relationships are understood.

3. CONCLUSIONS

The cationic polymerization of oxetane monomers initiated by bis cumyl chloride/silver antimony hexafluoride at -95°C under systematic monomer addition forms well defined alternating block polymers. Optimization of molecular structure is achieved by conducting the polymerization at $<-85^{\circ}\text{C}$, injecting the monomer in a continuous stream at a rate corresponding to 20% of the total monomer to be added per minute. Workup is easily achieved by washing the polymer solution after quench with concentrated ammonium hydroxide followed by precipitation from methyl alcohol.

4. ACKNOWLEDGEMENT

This work is supported by the Strategic Defense Initiative Organization/ Innovative Science and Technology; Contract N00014-87-C-0098; Scientific Officer, Dr. R. S. Miller.

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9. JANNAF Propulsion Meeting, San Diego, December 1987.

In addition to this work, we can now report a general synthesis procedure that we use to obtain triblock polymers with high specific blocking. Initial measurements of the degree of blocking at NWC by FT/NMR show that more than 96% of all monomers in the polymer are associated in a homopolymer block and the remaining monomers are at the block interface.

STANDARD PROCEDURE USED TO PREPARE BAMO-AMMO-BAMO THERMOPLASTIC ELASTOMER

All glassware used up to the time of reaction quench was dried in an oven at 110-120°C. A two-liter, three-neck, round-bottom flask was fitted, while hot (95°C), with a nitrogen gas inlet, a drying tube gas outlet, a stirrer, an RTD Thermocouple, and access for a monomer delivery tube. The flask was flushed with dry nitrogen gas while cooling to room temperature. Then, 1000 gm of dry (HPLC grade stored over molecular sieves) methylene chloride was weighed into a dry flask. Each monomer, 32 gm of AMMO and 4.2 gm of BAMO, was similarly weighed into separate 50 ml conical flasks.

When the reaction flask temperature was at room temperature, the flow of nitrogen was reduced and 80% of the total methylene chloride was added to the flask. The silver hexafluoro-antimonate (1.663 gm) was weighed out and immediately added to the reaction flask. The remaining methylene chloride was used to wash the funnel and weighing paper used for this addition.

The reaction flask was cooled to -95°C using a methanol-dry ice mixture. Liquid nitrogen was then added with stirring to lower the bath to near -100°C.

While the cooling was proceeding, the HPLC pump was prepared for use. The delivery tube was submerged for part of its length into a dry ice-methanol bath at -45 to -55°C to cool the monomers as they were pumped in. The di-cumylchloride (DCC) was weighed out (0.554 gm) and dissolved in 4 ml of dry methylene chloride and then injected into the flask. Immediately, the AMMO monomer was injected into the flask at a flow rate of 8 gm per minute. As the monomer was added, the flask temperature increased due to the reaction exotherm. Liquid nitrogen was added to the bath to counteract the temperature increase. Using this technique, the temperature change was -94.5°C at the start to -87.5°C near the end of the AMMO addition.

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At the end of the AMMO addition, the pump inlet tube was switched as quickly as possible to the BAMO flask, and the BAMO was pumped in using the same pump setting.

Three minutes after the end of the BAMO addition, the polymerization was quenched with 50 ml of a 50/50 v/v methanol/water solution. The cooling bath was removed, and 80 ml of concentrated ammonium hydroxide were added to the reaction flask and the resulting mixture warmed to room temperature. The reaction solution was transferred to a 2-liter separatory funnel and the aqueous layer removed. The polymer solution was washed with 3 x 200 ml of water, and the organic layer was dried over $MgSO_4$. After filtering through Celite, the volume of solvent was reduced under vacuum and then slowly added to a large excess (2 liters) of methanol with vigorous stirring. The stirring was continued for 30 minutes. The methanol was decanted off and the polymer washed twice, with vigorous stirring, using 200 ml of methanol with each wash.

The polymer was then placed in a desiccator under vacuum to dry.

By this method we have now completed three series of triblock polymers which initiates our study of structure/property relationships. The actual evaluation is being carried out at NWC with respect to rate of crystallization and mechanical properties.

Table 2 describes a series of polymers where the center block was maintained at constant molecular weight and the crystalline end blocks were varied.


Table 3 describes a series of polymers where the end blocks were maintained at constant weight and the amorphous center block was varied.

Table 4 is, in fact, an extension of Table 1 where the crystalline block molecular weight was reduced to almost zero.

Recent communication with NWC suggests some startling results with respect to block interaction on the rate of crystallization and morphology. As the work progresses, NWC will report to you their results.

Participating Personnel: R. W. Fletcher

Respectfully submitted,


G. E. Manser
Scientist
Chemical Research and Development

Enclosures: Tables 2, 3, and 4

cc: Phillip Miller, Consultant

TABLE 2
TPE
BAMO-AMMO-BAMO
NB-C727-29

TPE	Block	Theoretical Moles	Theoretical Grams	Actual Moles	Actual Grams	Theoretical MV (K)	Corrected Theoretical MV (K)	\bar{H}_a	\bar{H}_v	Q
29-A	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.013	2.1	0.013	2.1	0.875	0.875	36,534	50,151	1.37
	Total					15.24	15.24			
29-B	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.019	3.2	0.019	3.2	1.3	1.3	39,098	53,713	1.37
	Total					16.1	16.1			
29-C	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.025	4.2	0.024	4.1	1.75	1.71	41,266	57,461	1.39
	Total					17.0	16.9			
29-D	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.031	5.29	0.031	5.1	2.2	2.1	43,136	60,981	1.41
	Total					17.9	17.7			
29-E	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.038	6.35	0.036	6.1	2.5	2.5	46,035	64,112	1.39
	Total					18.8	18.6			
29-F	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.05	8.5	0.049	8.3	3.5	3.5	49,228	69,490	1.41
	Total					20.6	20.4			
29-G	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.06	10.6	0.06	10.1	4.4	4.2	61,552	97,021	1.58
	Total					22.3	21.9			
29-H	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.076	12.7	0.07	11.7	5.3	4.9	69,518	110,646	1.59
	Total					24.1	23.3			

TABLE 3

TPE

BAMO-AMMO-BAMO
NB-C727-30

TPE	Block	Theoretical Moles	Theoretical Grams	Actual Moles	Actual Grams	Theoretical MW (K)	Corrected Theoretical MW (K)	\bar{M}_n	\bar{M}_w	Q
30-A	AMMO	0.15	19.45	0.15	19.45	8.1	8.1			
	BAMO	0.036	6.0	0.036	6.0	2.5	2.5			
	Total					13.1	13.1	33,407	42,180	1.26
30-B	AMMO	0.2	25.8	0.2	25.8	10.8	10.8			
	BAMO	0.036	6.0	0.036	6.0	2.5	2.5			
	Total					15.8	15.8	41,285	55,339	1.34
30-C	AMMO	0.25	30.8	0.25	30.8	16.0	16.0			
	BAMO	0.029	4.8	0.028	4.75	2.5	2.5			
	Total					21.1	21.0	47,678	64,946	1.36
30-D	AMMO	0.25	31.7	0.25	31.7	18.7	18.7			
	BAMO	0.025	4.27	0.024	4.0	2.5	2.4			
	Total					23.7	23.5	53,237	74,125	1.39
30-E	AMMO	0.25	32.5	0.25	32.5	21.4	21.4			
	BAMO	0.023	3.8	0.022	3.7	2.5	2.45			
	Total					26.4	26.3	59,645	85,755	1.44
30-F	AMMO	0.26	33.2	0.26	33.2	23.7	23.7			
	BAMO	0.021	3.5	0.019	3.14	2.5	2.2			
	Total					28.7	28.1	59,634	84,195	1.41

TABLE 4
TPEBAHO-AMMO-BAHO
NB-C727-35

TPE	Block	Theoretical Moles	Theoretical Grams	Actual Moles	Actual Grams	Theoretical MV (K)	Corrected Theoretical MV (K)	\bar{N}_s	\bar{N}_v	Q
35-A	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.015	2.54	0.015	2.54	1.06	1.06			
	Total					15.6	15.6			
35-B	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.013	2.12	0.013	2.12	0.88	0.88			
	Total					15.3	15.3			
35-C	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.010	1.69	0.010	1.69	0.71	0.71			
	Total					14.9	14.9			
35-D	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.0076	1.27	0.0076	1.27	0.53	0.53			
	Total					14.6	14.6			
35-E	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.0050	0.85	0.0050	0.85	0.35	0.35			
	Total					14.2	14.2			
35-F	AMMO	0.25	32.38	0.25	32.38	13.5	13.5			
	BAMO	0.0025	0.42	0.0025	0.42	0.18	0.18			
	Total					13.9	13.9			